1Pp022 The mechanism of ferromagnetic coupling in Cu-Gd complexes: *ab inito* calculations and modeling

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This work offers the first series of the state of the art quantum chemical calculations (CASSCF, CASPT2, CASVB) and analytical models devoted to the well-known problem of quasi-general ferromagnetic coupling in copper-gadolinium complexes.[1,2] This phenomenon is frequently invoked in experimental literature, while it received up to date only qualitative theoretical explanations (Bencini *et al.*[3] suggested ligand polarization factors and Kahn[2] assumed the role of *3d→5d* one-electron jump between transition metal and lanthanide ion) Other theoretical studies of are scarce, the phenomenon being incompletely understood.[4,5]

A Cu-Gd complex due to Costes *et al.*[6] was taken as prototype. The CASSCF calculation on experimental structure gave 30.7 cm^{-1} ferromagnetic gap, extremely close to the experimental value 28 cm^{-1}. The molecule was further idealized imposing C_{2v} symmetry (with geometry optimization) taking then series of systematic changes of active space and other computation conditions. The calculations were conducted in non-standard manner, in order to tackle the non-*aufbau* basic electron configuration, with the half-occupied *f*-shell contracted below many ligand-double occupied MOs. As is shown in table, the ferromagnetic coupling is intrinsic to Cu-Gd, while the inclusion of ligand states and the enhancement of active space on Gd ion are increasing its magnitude.

Table I. Illustrative quantities for Cu-Gd systems (computed ferromagnetic gap, its mono- and bi-electronic dichotomy, The series includes in progressive manner the ligand role.

System Method	"Naked" Cu-Gd (CI, CASSCF)	Cu-Gd Ligand as EFP (CI, CASSCF)	CuL-Gd CI-only	CuL-Gd CI-only	CuL-Gd CASSCF
Active Space	$d_{Cu}+(f^7sd^5)_{Gd}$	$d_{Cu}+(f^7sd^5)_{Gd}$	$d_{Cu}+(f^7)_{Gd}$	$d_{CuL}+(f^7sd^5)_{Gd}$	$d_{CuL}+(f^7sd^5)_{Gd}$
$\mathbf{\Delta E_{ferro} = 4J}$	0.02	0.30	0.40	2.95	12.02
One-electron	+0.22	+5.07	-0.83	+37.03	+72.67
Bielectronic:	-0.20	-4.77	+1.23	-34.08	-60.645

The extraction from *ab initio* data and analytical modeling of significant molecular integrals showed that, in the discussed conjecture, the Kahn's mechanism may account for 20% of the total CI contributions to the ferromagnetic gap. In turn, the CI with excided states with due to $f^7 \rightarrow f^6 d$ promotions on Gd, or its f^7 sextet states in the case of low spin wave function, revealed a surprising relative importance. The CASPT2-type MOs playing the role of effective magnetic orbitals in the given problem are displayed in the figure 1.

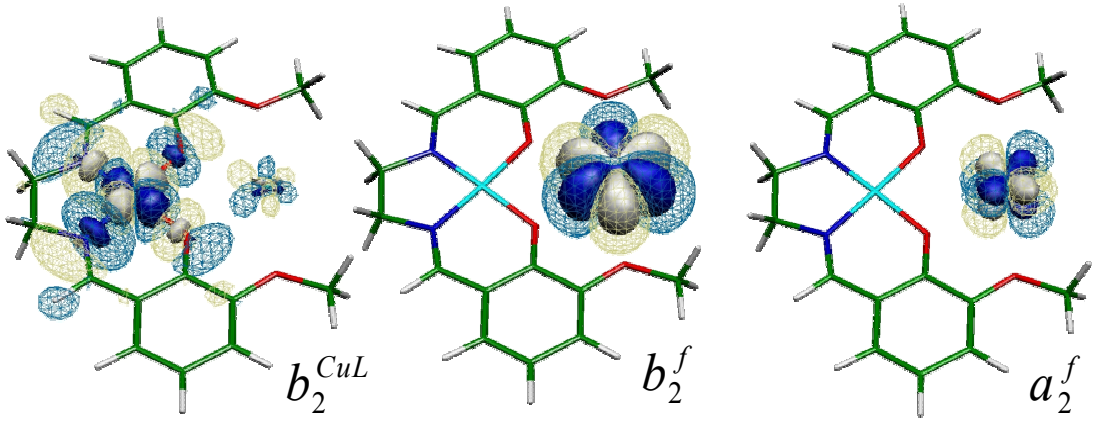

Figure 1. Natural MOs for CuLGd system, from CASPT2 calculation

The whole mechanism can be further rationalized, within a new formalism, in terms of symmetry determined orthogonality between spectral terms corresponding to the local configurations of metal ions. Indeed, in C_2 or C_{2v} symmetry, the local states on *d*-transition metal and lanthanide ions have the different irreducible representations, conditioning the ferromagnetic coupling. A review of various experimental structures shows that, indeed, the C_{2v} pseudo-symmetry occurs at coordination sites, providing then a general explanation for the widespread ferromagnetic effect. The antiferromagnetic exceptions occur when the molecular asymmetry is advanced and the usual configuration interaction forces are overriding the intrinsic ferromagnetic part.

References.

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